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# A Method for the Determination of Halogens in Organic Compounds

# A METHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

BY

JOHN FREDERICK LEMP

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## THESIS

FOR THE

## DEGREE OF BACHELOR OF SCIENCE

IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

John Frederick Lamp

ENTITLED A Method for the Determination of Halogens in Organic Compounds

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

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# INTRODUCTION

The growth and the importance of the field of Organic Chemistry has induced a similar growth in the study and the establishment of methods of analysis with which to prove the structures and test the purities of the various compounds. At the present time, however, very few books exist which deal with the systematic analysis of organic substances. Fewer still are the reliable methods of analysis which may be applied to all types of organic compounds. The work covered in this thesis deals with several types of compounds containing halogens. The chief object having been to get an accurate, rapid and economical method for the quantitative determination of halogens.

Articles on at least a dozen different methods for the estimation of halogens are to be found in the various journals.[1] Very few of these methods are in general use. According to Clarke,[2] the Carius method is most widely used. If the experiments are not carefully conducted this method may result in dangerous explosions owing to the high pressures developed within the sealed glass tubes which are used. It requires also considerable time but is applicable to practically all types of organic halogen compounds and gives excellent results.

S. W. Parr[3] and H. H. Pringsheim[4] have published a number of articles on the use of sodium peroxide in halogen determinations. They have shown that sodium peroxide has many advantages in both qualitative and quantitative organic analysis. Delbridge[5] claims to have gotten unsatisfactory results with the method of Pringsheim.[4] He recommends a modification of the lime method as giving the desired results in hundreds of determinations where it has been tried. In the latter method a combustion with lime is carried on in a Jena glass tube. After combustion the contents of the tube is transferred to an Erlenmeyer flask, dissolved in dilute nitric acid and the chlorine present precipitated by means of a tenth normal solution of silver nitrate. The precipitate is finally filtered and washed with dilute nitric acid and the filtrate titrated with a standard ammonium thiocyanate solution according to Volhard. Sodium peroxide, however, is not limited to the qualitative and quantitative estimation of halogens alone. Parr[3] has made the reagent applicable to the determination of both arsenic and sulphur in the inorganic compounds. Pringsheim[4] also refers to its use in the analysis of organic compounds of sulphur, phosphorus and arsenic. In fact, the excellent qualitative and quantitative results obtained by Parr[3] and Pringsheim[4] indicate that as a substitute for a number of methods, especially that of Carius for decomposing organic compounds of the halogens, the peroxide fusion is in every way to be preferred. The direct object has been to perfect a method whereby a standard fusion cup could be used

in the determination of halogens in organic compounds. This led to a repetition of some of the work of Pringsheim and an alteration in the method, which makes it possible to make accurate determinations, particularly in the iodides. As will be emphasized later, several things have been overlooked in previous work on the determination of iodine.

## EXPERIMENTAL

The compounds first worked with were the organic chlorides. Since a thorough mixture of all the ingredients of the charge is absolutely essential in obtaining good results, all details must be carefully noted. Approximately ten grams of sodium peroxide and from one to one and one half grams of very finely ground potassium nitrate are first thoroughly mixed in a Parr sulphur bomb.[6] This bomb is a tightly sealed steel alloy cup, a cross section of which is shown in the following figure. From .4 to .45 of a gram of benzoic acid or sugar is now added and the whole mass again thoroughly mixed. Finally add .2 to .25 of a gram of the compound and mix once more being careful at all times not to lose any of the contents of the cup. For volatile liquids the difficulty of securing an accurate weight of the material taken is met by the following procedure. A light bulb weighing .2 of a gram or less and having a capillary tip is blown of approximately the size and shape shown in figure 2.

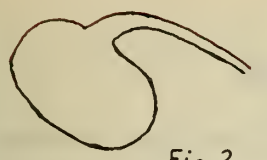

Fig. 2

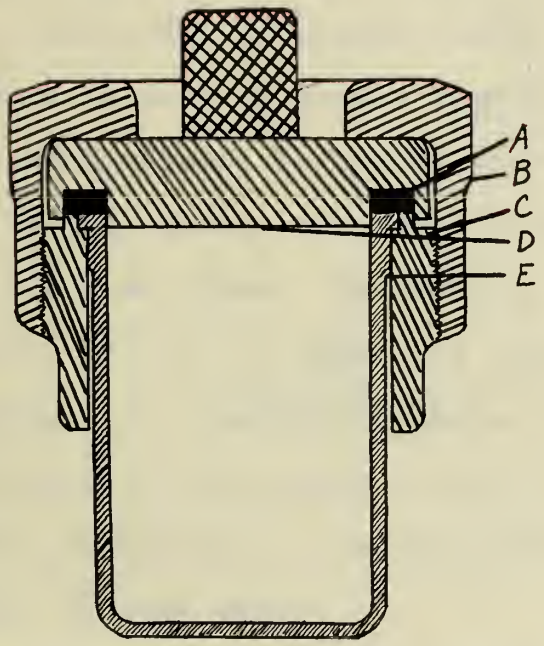


Fig. 1

# The Parr Sulphur Bomb.

A — Rubber Gasket.
B — Screw Cap.
C — Screw Collar.
D — Cover.
E — Cup.

Thin walled glass tubing of about 5/32 inch in diameter may be used for this purpose. Weigh the bulb carefully. Now dip the capillary end into the liquid and by alternate gentle warming and cooling draw the liquid into the bulb. When about .2 of a gram is obtained, seal the capillary in the flame and weigh accurately. From this point on the procedure is the same as given above. The bulb, of course, being broken after sealing the bomb. This is done by gently tapping the bomb on the table. The cup should always be tapped lightly after sealing to get the material to the bottom. The mass is then fused over the hottest part of a Bunsen flame. The heating should be continued until the cup is red for at least one fourth its length. The bomb and its contents is immediately cooled under the water tap. After opening the bomb, the cover is first washed off with hot water catching the washings in a beaker containing approximately two hundred cc. of warm water.

Now place the cup into the beaker and cover with a watch glass. After the violent frothing has ceased, heat the solution just to boiling, remove the cup, and wash any adhering liquid back into the beaker. The solution is now digested for at least three minutes to thoroughly decompose any sodium peroxide. Acidify with concentrated nitric acid and boil to help dissolve all the iron as well as drive off all carbon dioxide. Cool the clarified solution and precipitate with a measured excess of .1 normal silver nitrate. With a thorough

breaking down of the larger particles and the coagulation of the precipitate by gentle boiling, it has been found unnecessary to filter off the silver chloride.[7] The solution is again cooled and the excess of silver nitrate determined by the Volhard method using a .1 normal solution of ammonium thiocyanate for the titration and ferric alum as an indicator. The above procedure is almost identical with that used by E. R. Brunskill.[8]

Bromine was then determined in the same way. It was found, however, that it gave results which did not even check with each other when run in duplicate showing that the fault did not lie with the impurity of the organic compound. It is, of course, well known that hydriodic acid is easily oxidized by nitric acid giving free iodine. Upon boiling an acidified solution from an iodide fusion, free iodine could actually be seen coming off showing that in both bromine and iodine a reaction similar to the following probably took place,-

$$2HNO_3 + 2HI \longrightarrow 2NO_2 + I_2 + 2H_2O$$

This seems to be in direct contradiction to the work of Pringsheim[4] in which he claims to have gotten excellent results by directly acidifying the alkaline solution with nitric acid. It may be, however, that with only a slight excess of nitric acid and no boiling that such a reaction might not take place. Such a procedure, i.e. only a very slight excess of acid and no boiling could not be followed in this work because, as was mentioned before, of the large amount of precipitated iron obtained in each case. There is, of course, a possibility of filtering but it

would require much time since in most cases the precipitate was quite large. Another possibility for overcoming the difficulty and one which was found to give the desired results is represented by the following equation:

Fusion

$$\left.\begin{array}{l} Na_2O_2 \\ *C_6H_5CO_2H \text{ or } C_{12}H_{22}O_{11} \\ KNO_3 \\ RI \end{array}\right\} + H_2O \xrightarrow{\text{boil}} \left\{\begin{array}{l} Na_2CO_3 \\ NaOH \\ K_2CO_3 \text{ etc.} \\ NaI \\ NaIO_3 \dagger \end{array}\right.$$

$$\left.\begin{array}{l} **\\ AgNO_3 \\ + \\ \text{digest} \end{array}\right\} \longrightarrow \left\{\begin{array}{l} Ag_2CO_3 \\ Ag_2O \\ AgI \\ AgIO_3 \text{ , etc.} \\ Na_2CO_3 \\ NaOH \\ K_2CO_3 \\ NaNO_3 \end{array}\right. + HNO_3 \longrightarrow \left\{\begin{array}{l} AgNO_3 \\ AgI \\ AgIO_3 \\ NaNO_3 \\ KNO_3 \end{array}\right.$$

* A slight modification of the former charge has been made, i.e. the amount of organic compound to be used is to be kept as near .2 of a gram as possible and to this is added from .4 to .45 of a gram of benzoic acid or finely ground sugar. These quantities are flexible within certain limits, though the total amount of organic combustible should not greatly exceed .5 or .6 of a gram. This addition of compounds high in carbon and hydrogen though necessary only with the more highly halogen-

ated compounds is advisable in all charges in order to insure thorough and uniform fusion,the latter having been found essential to good results.

† Due to the excess of sodium peroxide in the fusion cup some of the sodium iodide formed will be oxidized to the iodate or one of the other oxyacids.

**The alkaline solution plus silver nitrate must be digested to thoroughly coagulate all silver iodide.

Silver iodate and the other oxyacids of iodine, which may be present in the solution are soluble in hot water and in nitric acid and must first be reduced to silver iodide and water before the titration with ammonium thiocyanate. To find the proper reducing agent has been quite a problem. Alcohol, sodium sulphite, magnesium and zinc have all been suggested. Alcohol seems to form too many side reactions which prevent a good titration. In each case where alcohol was tried there were dark colorations, liberation of excessive oxides of nitrogen and aldehyde formations. Sodium sulphite when used in quantities large enough to insure complete reduction almost invariably gave high results. When added only in small quantities the results were low. The high results may be due to the formation of some silver sulphate which is not all dissolved by the amount of nitric acid present. There may also be some possibility of a partial reduction of silver nitrate to free silver during some stage of the reaction. Metallic magnesium and zinc were found to generate plenty of hydrogen in the acid solution to entirely reduce the iodate to iodine and water but the reaction seemed to

go in the following direction,-

$$2AgIO_3 + 5H_2 + 2HNO_3 \longrightarrow 2AgNO_3 + 6H_2O + I_2$$

Considering iodine as having five plus charges in a compound such as $NaIO_3$ and considering the reaction as going on by steps this reduction might be represented as follows,-

$$I \xrightarrow{5+} I \xrightarrow{4+} I \xrightarrow{3+} I \xrightarrow{2+} I^{+} \longrightarrow I$$ where the reduction stops thus liberating free iodine.

Silver bromate or the other oxyacids of bromine can be precipitated with either zinc or magnesium, i.e., the following reaction probably takes place,-

$$AgBrO_3 + 3H_2 \longrightarrow AgBr + 3H_2O$$

But silver bromate does not form in every case- in fact, it was seldom found necessary to add a reducing agent to any of the bromine fusions.

The addition of a reducing agent is recommended, however, in order to be certain that no bromine is lost.

Hydrazine sulphate was the next reducing agent tried. It is added slowly to the hot acidified solution containing the precipitated silver halide as indicated below,-

$$\left.\begin{matrix} AgNO_3 \\ AgI \\ AgIO_3 \\ NaNO_3 \\ KNO_3 \end{matrix}\right\} \text{boil gently} + N_2H_4.H_2SO_4 \longrightarrow \left\{\begin{matrix} AgI \\ AgNO_3 \\ NaNO_3 \\ KNO_3 \\ Na_2SO_4 \end{matrix}\right.$$

If an oxyacid of either bromine or iodine is present there will be an immediate evolution of gas which is nitrogen and a precipitation of the silver salt, thus,-

$$15N_2H_4 . H_2SO_4 + 10AgIO_3 \longrightarrow$$
$$10AgI + 15N_2 + 15H_2SO_4 + 30H_2O$$

Hydrazine sulphate is added slowly with stirring until reaction ceases. No frothing indicates the absence of the oxyacids. This was the only reliable reducing agent found for the iodates and its use is also recommended for bromates in preference to either magnesium, zinc or sodium sulphite. Results of the determinations made are given in the following table,-

| Compound | Amount taken in grams | Per cent Halide Calculated | Per cent Halide Found |
|---|---|---|---|
| Naphthalene Sulphone Chloride ($C_{10}H_7SO_2Cl$) | .3804 | 15.65 | 14.27- |
| | .2919 | 15.65 | 14.45- |
| Nitro-Benzyl Chloride ($NO_2C_6H_4CH_2Cl$) | .3809 | 20.67 | 20.47 |
| | .3804 | 20.67 | 20.08 |
| Chlor-Benzoic Acid ($ClC_6H_4CO_2H$) | .2500 | 22.65 | 22.32 |
| | .1848 | 22.65 | 21.86° |
| Pyridine Hypo Chloride ($C_6H_5NHCl$) | .3889 | 30.69 | 28.82° |
| | .3776 | 30.69 | 30.61 |
| Phenylen-diaminchlor-hydrat ($C_6H_4(NH_2)_2$-2HCl) | .2418 | 39.17 | 39.06 |
| | .2244 | 39.17 | 39.90 |
| Chlor-nitro-benzene ($C_6H_4NO_2Cl$) | .3010 | 22.95 | 22.41- |
| | .2778 | 22.95 | 22.41- |
| P-bromo acetanilide ($C_8H_7NHOBr$) | .2862 | 37.34 | 37.30 |
| | .3200 | 37.34 | 37.02 |
| Di-brom-benzene ($C_6H_4Br_2$) | .3896 | 67.76 | 67.61 |
| | .3859 | 67.76 | 60.01° |
| Brom-phenol ($BrC_6H_4OH$) | .3551 | 46.20 | 45.58° |
| | .4593 | 46.20 | 46.95 |
| Brom-benzoic acid ($BrC_6H_4CO_2H$) | .2791 | 39.76 | 39.63 |
| | .2744 | 39.76 | 39.17 |
| | .2761 | 39.76 | 39.98 |
| Tri-phenyl-chlor-methane ( $(C_6H_5)_3 \geqq C$-Cl) | .2762 | 12.72 | 12.81 |
| | .2808 | 12.72 | 12.79 |
| P-bromo sulfonyl derivative of arsanilic acid $Br(C_6H_4)_2NHSO_2AsO_3H_2$ | .2745 | 18.32 | 18.60 |
| Tetra-bromo-benzoquinone ($C_6Br_4O_2$) | .2000 | 75.45 | 74.28* |
| | .2852 | 75.45 | 74.04* |
| Di-nitro-di-brom-benzene ($C_6H_2(NO_2)_2Br_2$) | .2801 | 49.04 | 50.14* |
| | .2803 | 49.04 | 49.73* |

| Compound | Amount taken in grams | Per cent Halide Calculated | Per cent Halide Found |
|---|---|---|---|
| Iodoform ($CHI_3$) | .2000 | 96.65 | 96.50 |
| | .2000 | 96.65 | 96.90 |
| P-chloro-toluene ($ClC_6H_4CH_3$) | .2380 | 28.02 | 27.71- |
| | .2378 | 28.02 | 27.70- |

Results obtained by E. R. Brunskill,[8]-

| | | |
|---|---|---|
| P-chlorobenzoylacetic ester $C_{11}H_{11}O_3Cl$ | 15.67 | 15.79 |
| P-chlorobenzoylacetic acid $C_9H_7O_3Cl$ | 17.88 | 17.89 |
| Phenacyl-p-chlorobenzoylacetic ethyl ester $C_{19}H_{17}O_4Cl$ | 10.33 | 10.36 |
| 4-Chlorodiphenacyl $C_{16}H_{13}O_2Cl$ | 13.02 | 13.28 |
| P-chlorophenacylbenzoylacetic ethyl ester $C_{19}H_{17}O_4Cl$ | 10.33 | 10.58 |

Contrary to the results obtained by G. Dreschsel[9] and later confirmed by M. A. Rosanoff[9] and A. E. Hill[9] most all chlorine percentages in the above table are lower and not higher than the theoretical. Since, however, the coagulation of silver chloride by boiling, as described by V. Rothmund[7] and A. Burgstaller, was used in all these experiments it is safe to say that no discrepancy in the percentages can be attributed to the Volhard method of titration. This, I believe, holds true not only for the chlorine, but also for the bromine and iodine since particular care was taken in every case to break up all large adhering particles by a thorough digestion thus preventing the precipitate from enclosing either soluble chloride, iodide or silver nitrate. Then too in the procedure followed in determining iodoform there is not much chance of an appreciable amount of the silver iodide going into solution as suggested by Clarke.[10]

Hence, since the errors in the above table did not originate from the method of titration they must have come from one or all three other sources, namely,- (1) poor fusions, (2) impure reagents, (3) impure organic compounds. Small mechanical losses are, of course, unavoidable but in most cases these are negligible as compared with the other three. All results which vary and are most likely due to poor fusions are marked (O) in the above table. All benzoic acid used in the fusions contained small amounts of halogens but this impurity did not run uniform. This was partially overcome by a thorough mechanical mixing. Blank fusions then run upon the acid gave the necessary

corrections. The latter, however, when applied to the regular determinations did not give as good results as was hoped for. Results where benzoic acid was used in the charge are marked (*) in the table. It is highly probable that in the results marked (-), the differences between the halide found and the theoretical are due to slight impurities in the organic compounds.

## INTERPRETATION OF RESULTS

The results on the whole show the above procedure to be reliable when all details are closely adhered to. Upon studying the table it will be seen that a good fusion is absolutely essential in obtaining reliable results. Sugar is to be preferred to benzoic acid for getting a good fusion when the latter is found to contain any trace of halogens. At the present time sugar is also likely to be more economical. Other points to be closely noted are,-

(1) Total precipitation using an excess of silver nitrate. If there is not an excess of silver nitrate some of the halide will be liberated during the procedure to follow. A violet colored solution which sometimes appears during some part of the digestion should not be mistaken for an escaping halogen. This color is sometimes caused by manganese which is in the alloyed steel of the fusion cup. It may be removed by the continued boiling of the acid solution or by the addition of a small amount of hydrogen peroxide.

(2) Thorough digestion and coagulation whenever it is called for in the outline given. This is to produce a total precipitation, prevent inclusions, etc.

(3) Total reduction of all oxy-acids such as the bromates, iodates, etc.

(4) Careful manipulation. Beakers should be carefully covered with watch glasses at all times when there is danger of loss by bumping or frothing.

It was noticed that in the case of chlorine and iodine the best results are obtained when the determinations are run in as short a period as possible, giving, however, plenty of time for the various reactions to take place. From four to eight duplicate determinations may be run within five or six hours depending all together upon the speed and skill of the worker. Though only one liquid was run the results obtained on the P-chloro-toluene show that this method is applicable alike to volatile and non-volatile compounds. The variety of compounds used also seems to prove that the method is reliable for all the halogen compounds regardless of the degree or type of halogenation.

## SUMMARY

The chlorides, bromides and iodides of a variety of organic compounds have been quantitatively determined by fusion with sodium peroxide in a Parr[6] sulphur bomb. The essential

points for obtaining correct results were found to be,-

(1) A thorough and uniform fusion.

(2) The addition of an excess of silver nitrate to the alkaline solution and the thorough coagulation by gentle boiling of any silver halide which may be formed at this point.

(3) The addition of enough of some reducing agent to cause a rapid and total reduction of any oxy-acids which may have been formed. Hydrazine sulphate was found to be better than any other which was tried.

The Volhard method of titration has been used for the excess silver nitrate determination. This procedure is applicable to the highly halogenated and volatile compounds as well as all others.

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